Thermoacoustical response of 1,4-dioxane with carboxylic acids

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Experimental values of ultrasonic velocity (u), density (ρ), refractive index (n) and viscosity (η) for the binary mixtures of 1,4-dioxane with acetic acid and propionic acid have been measured at 293, 303 and 313 K over the entire mole fraction range. Using these data, the excess adiabatic compressibility (β_s^E), deviation in viscosity ($\Delta\eta$), excess intermolecular free length (L_f^E), molar compressibility (B), molecular radius (r_m), relaxation strength (r), and van der wall's constant (b) have been calculated. These parameters were used to study the nature and extent of intermolecular interaction between component molecules present in the binary mixtures. Excess values of β_s and η were plotted against the mole fraction of 1,4-dioxane over the whole composition range. The values of β_s^E, $\Delta\eta$ and L_f^E for two binary mixtures have been found to be negative which suggest the presence of weak molecular interaction in these mixtures. Molecular radius (r_m) and relaxation strength (r) of liquid mixtures were also evaluated since these parameters are useful in prediction of molecular properties of liquid mixtures.

Keywords: 1,4-Dioxane; Acetic acid; Propionic acid; Excess adiabatic compressibility; Viscosity deviation

1. Introduction

Ultrasonic investigation of binary liquid mixture has revolutionized the world of medical petrochemical and pharmaceutical industries to a great extent [1–4]. The ultrasonic measurements have been widely used to study the molecular structure and molecular interaction mechanism of the matter. Ultrasonic velocity and adiabatic compressibility of liquid mixtures are useful in understanding the solute–solvent interactions [5,6] and investigating the physico-chemical behaviour of liquid mixtures. Excess properties provide valuable information about the molecular interactions and macroscopic behaviour of liquid mixtures, and can be used to test and improve thermodynamical models for calculating and predicting the fluid phase equilibria [7–10].

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The knowledge of excess adiabatic compressibility helps in understanding the molecular orientation and to study the extent of intermolecular interaction between component molecules of the liquid mixtures [11].

1,4-Dioxane cyclic ether is used as a degreasing agent, as a component of paint and varnish removers, and as a wetting and dispersion agent in the textile industry. Dioxane is also used as a solvent in the chemical synthesis. Ultrasonic studies of the solution of the carboxylic acids with dioxane [12] have yielded valuable information regarding the association between the monomers of carboxylic acid and free oxygen of dioxane through hydrogen bonding.

In order to examine molecular interactions, we report here the ultrasonic velocity (u), density (ρ), refractive index (n) and viscosity (η) of binary mixtures of 1,4-dioxane (D) with acetic acid (AA) and propionic acid (PA) over entire composition range at varying temperatures of 293, 303 and 313 K. The experimental values of u, ρ, n and η were used to calculate excess adiabatic compressibility (β_s^E), viscosity deviation ($\Delta\eta$), excess intermolecular free length (L_f^E), molar compressibility (B), molecular radius (r_m), relaxation strength (r) and van der wall's constant (b). These parameters are quite sensitive towards the interactions between the component molecules in the mixtures. The dependence of these parameters on composition of the mixtures reveals the nature and extent of interaction between component molecules.

2. Experimental details

Ultrasonic velocity was measured using the ultrasonic interferometer (model M 83) supplied by Mittal Enterprises, New Delhi that has reproducibility of $\pm 0.4\,\mathrm{m\,s^{-1}}$ at 25°C.

The density has been measured using a pyknometer with an accuracy of $\pm 0.5\,\mathrm{kg\,m^{-3}}$. The pyknometer consists of a long tube graduated in 0.01 mL scale, fitted to a specific gravity bottle of capacity of 8 mL.

Refractive index was measured using Abbe's refractometer provided by Optics Technologies, New Delhi. The refractometer was calibrated by measuring the refractive indices of triple distilled water and benzene at $T = 293$ K. The accuracy in the refractive index measurement was 0.001 unit.

The viscosity of the mixtures was determined by using Ostwald's viscometer which was kept inside a double wall jacket in which water from thermostatic water bath was circulated. The inner cylinder of this double wall glass jacket was filled with the water of desired temperature so as to establish and maintain thermal equilibrium. The accuracy in the viscosity measurements is within $\pm 0.5\%$.

Mixtures were prepared by weighing the liquids in specially designed ground glass stopped bottles, taking extreme precautions to minimize preferential evaporation. A Sartorius (BP 121S) single-pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction is estimated to be ± 0.0001.

The chemicals used were obtained from Ranbaxy Fine Chemicals Limited. All the chemicals used were purified by standard procedure, discussed by Perrin and Armarego [13]. All the samples were kept in tightly sealed bottles to minimize the absorption of atmospheric moisture.

2.1. *Theory*

The fundamental relation for obtaining the excess values of any parameter 'A' is given by

$$A^{\mathrm{E}} = A_{\mathrm{exp}} - A_{\mathrm{ideal}} \tag{1}$$

where A_{exp} = experimentally determined value of A.

A_{ideal} = expected value of A with ideal mixing approximation.

Literature survey [14,15] reveals that A_{ideal} is calculated as the mole fraction average of the value of parameter A for pure components, i.e.

$$A_{\mathrm{ideal}} = \sum x_i A_i = x_1 A_1 + x_2 A_2 \ \text{(for binary mixtures)} \tag{1a}$$

For adiabatic compressibility $\beta_{\mathrm{s}}^{\mathrm{E}}$, Laplace's equation gives

$$A_{\mathrm{exp}} = \beta_{\mathrm{exp}} = \frac{1}{u^2 \rho} \tag{2a}$$

and

$$A_i = \beta_i = \frac{1}{u_i^2 \rho_i^2} \tag{2b}$$

for viscosity deviation $(\Delta\eta)$

$$A_{\mathrm{exp}} = \eta \tag{3a}$$

and

$$A_i = \eta_i \tag{3b}$$

for excess intermolecular free length $(L_{\mathrm{f}}^{\mathrm{E}})$

$$A_{\mathrm{exp}} = L_{\mathrm{f\,exp}} = k\beta_{\mathrm{exp}}^{-1/7} \tag{4a}$$

$$A_i = L_{\mathrm{fi}} = k\beta_i^{-1/7} \tag{4b}$$

Using equations [(1a)–(4b)], we get the following standard equations

$$\beta_{\mathrm{s}}^{\mathrm{E}} = \frac{1}{u_i^2 \rho_i} - \left[\frac{x_1}{u_1^2 \rho_1} + \frac{x_2}{u_2^2 \rho_2} \right] \tag{5}$$

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{6}$$

$$L_{\mathrm{f}}^{\mathrm{E}} = k\beta_i^{-1/7} - \left[x_1 k\beta_1^{-1/7} + x_2 k\beta_2^{-1/7} \right] \tag{7}$$

where u, ρ, η denote the ultrasonic velocity, density and viscosity of mixtures respectively. u_i, ρ_i and η_i $(i=1,2)$ denote respectively the ultrasonic velocity, density and viscosity of ith component and k is Jacobson constant [9].

The molar compressibility (B), molecular radius (r_m) and relaxation strength (r) were determined using the following relations:

$$B = V_m \beta^{-1/7} \tag{8}$$

and

$$r_m = \left(\frac{3b}{16\pi N_A}\right)^{1/3} \tag{9}$$

Where b is a van der wall's constant which was estimated by

$$b = \frac{4V_m(n_{mix}^2 - 1)}{n_{mix}^2 + 2} \tag{10}$$

$$r = 1 - \left(\frac{u}{u_\infty}\right)^2 \tag{11}$$

where N_A, n and V_m denote avogadro number, refractive index and molar volume. u_∞ is taken $1600 \, \mathrm{m \, s^{-1}}$.

3. Results and discussion

The experimental values of ultrasonic velocity (u), density (ρ) at three temperatures viz. $T = 293$, 303 and 313 K along with the calculated values of molar compressibility (B), excess intermolecular free length (L_f^E), molecular radius (r_m), relaxation strength (r) and van der wall's constant (b) are given in tables 1 and 2 for (D + AA) and (D + PA) mixtures respectively.

The values of β_s^E and $\Delta\eta$ are plotted against the mole fraction of dioxane and are shown in figures 1(a) and (b) and 2(a) and (b) respectively.

The important effects which are expected to contribute to the value of excess functions in the present work are arbitrarily divide into physical, chemical and structural contributions:

(1) Physical contributions comprise non-specific physical interactions.
(2) Chemical effects occur due to the breaking up of the liquid order of associated species.
(3) Structural effects take place due to the geometrical fitting of dioxane and acetic acid and (or propionic acid) into the voids created by each other and also due to differences in molar and free volumes of these components.

Each factor makes positive or negative contribution to the resultant values of excess function and the magnitude of the contribution is dependent on mole fraction range [12].

The sign and magnitude of excess adiabatic compressibility (β_s^E) play an important role in assessing the molecular interactions between the component molecules in the liquid mixtures. β_s^E has been found to be negative for both the binary mixtures, over the whole mole fraction range (figure 1a and b). Negative values of β_s^E suggest that the structure is less compressible than the corresponding ideal mixture, suggesting that

Table 1. Ultrasonic velocity (u), density (ρ), excess intermolecular free length (L_f^E), molar compressibility (B), molecular radius (r_m), relaxation strength (r) and van der wall's constant (b) for (D + AA) mixture with mole fraction of dioxane (x_1) at temperature T.

S. no.	x_1	u (m s^{-1})	ρ (g cm^{-3})	L_f^E (A)	B (MKS)	r_m (nm)	r	b (cm^3 mol^{-1})
$T = 293$ K								
1	0.0000	1195	1.0492	0.0000	1170.72	0.1728	0.4422	52.03
2	0.0704	1214	1.0478	−0.0033	1216.04	0.1755	0.4243	54.47
3	0.1456	1232	1.0464	−0.0057	1264.16	0.1782	0.4071	57.07
4	0.2261	1251	1.0450	−0.0077	1315.33	0.1810	0.3887	59.83
5	0.3124	1270	1.0435	−0.0096	1371.58	0.1840	0.3700	62.84
6	0.4053	1289	1.0419	−0.0106	1431.26	0.1871	0.3510	66.05
7	0.5262	1312	1.0401	−0.0111	1509.28	0.1909	0.3276	70.24
8	0.6139	1328	1.0388	−0.0111	1566.02	0.1937	0.3111	73.27
9	0.7316	1347	1.0372	−0.0101	1641.80	0.1972	0.2912	77.35
10	0.8599	1361	1.0355	−0.0066	1722.55	0.2009	0.2764	81.78
11	1.0000	1368	1.0338	0.0000	1808.20	0.2048	0.2690	86.63
$T = 303$ K								
1	0.0000	1174	1.0450	0.0000	1168.82	0.1728	0.4616	51.99
2	0.0704	1190	1.0438	−0.0025	1213.12	0.1754	0.4468	54.42
3	0.1456	1207	1.0426	−0.0050	1260.76	0.1782	0.4309	57.01
4	0.2261	1225	1.0413	−0.0071	1311.42	0.1810	0.4138	59.76
5	0.3124	1243	1.0400	−0.0091	1367.12	0.1840	0.3965	62.77
6	0.4053	1261	1.0386	−0.0103	1426.23	0.1870	0.3789	65.97
7	0.5262	1282	1.0369	−0.0107	1503.22	0.1909	0.3580	70.14
8	0.6139	1297	1.0358	−0.0107	1559.35	0.1936	0.3429	73.17
9	0.7316	1314	1.0343	−0.0094	1634.04	0.1971	0.3255	77.23
10	0.8599	1327	1.0328	−0.0060	1713.92	0.2008	0.3121	81.65
11	1.0000	1335	1.0313	0.0000	1799.36	0.2047	0.3038	86.48
$T = 313$ K								
1	0.0000	1152	1.0425	0.0000	1164.95	0.1726	0.4816	51.88
2	0.0704	1167	1.0412	−0.0019	1208.93	0.1753	0.4680	54.30
3	0.1456	1184	1.0400	−0.0042	1256.54	0.1780	0.4524	56.90
4	0.2261	1202	1.0387	−0.0061	1307.17	0.1809	0.4356	59.64
5	0.3124	1221	1.0373	−0.0083	1363.15	0.1849	0.4176	62.65
6	0.4053	1241	1.0359	−0.0098	1422.77	0.1869	0.3987	65.85
7	0.5262	1263	1.0342	−0.0101	1500.13	0.1908	0.3770	70.02
8	0.6139	1278	1.0331	−0.0100	1556.47	0.1935	0.3615	73.04
9	0.7316	1297	1.0316	−0.0087	1631.69	0.1970	0.3429	77.10
10	0.8599	1313	1.0300	−0.0055	1712.69	0.2007	0.3266	81.52
11	1.0000	1325	1.0285	0.0000	1799.69	0.2046	0.3142	86.36

there may be intermolecular hydrogen bonding between ether and acids. This is in accordance with a view proposed by Fort and Moore [16] according to which liquids of different molecular size usually mix with decrease in volume yielding negative β_s^E values. Negative trends in β_s^E have been reported earlier for binary mixtures of THF with 1-propanol [9] and alcanols with alkanes [17].

Viscosity deviation ($\Delta\eta$) is found to be negative for both the binary mixtures over the entire composition range at all the three temperatures, which suggest the presence of weak intermolecular interaction. It can be seen from figure 2(a) and (b) that in both the mixtures, absolute values of $\Delta\eta$ decreases as temperature is raised. An increment of temperature diminishes the self association of the pure component and also the heteroassociation between unlike molecules, because of the increase of the thermal energy. This lead to less negative values of $\Delta\eta$ as temperature is raised as observed in

Table 2. Ultrasonic velocity (u), density (ρ), excess intermolecular free length (L_f^E), molar compressibility (B), molecular radius (r_m), relaxation strength (r) and van der wall's constant (b) for (D + PA) mixture with mole fraction of dioxane (x_1) at temperature T.

S. no.	x_1	u (m s^{-1})	ρ (g cm^{-3})	L_f^E (A)	B (MKS)	r_m (nm)	r	b (cm^3 mol^{-1})
$T = 293$ K								
1	0.0000	1186	0.9940	0.0000	1509.46	0.1901	0.4505	69.21
2	0.0854	1204	0.9980	−0.0022	1535.32	0.1914	0.4336	70.70
3	0.1737	1223	1.0019	−0.0040	1562.04	0.1928	0.4161	72.24
4	0.2649	1241	1.0059	−0.0055	1589.67	0.1942	0.3981	73.83
5	0.3592	1260	1.0099	−0.0065	1618.27	0.1956	0.3796	75.47
6	0.4567	1280	1.0138	−0.0072	1647.87	0.1971	0.3604	77.17
7	0.5577	1299	1.0178	−0.0075	1678.54	0.1986	0.3406	78.93
8	0.6623	1319	1.0218	−0.0073	1710.21	0.2001	0.3202	80.75
9	0.7708	1338	1.0258	−0.0062	1742.78	0.2016	0.3007	82.64
10	0.8833	1354	1.0298	−0.0037	1775.26	0.2032	0.2839	84.60
11	1.0000	1368	1.0338	0.0000	1808.20	0.2048	0.2690	86.63
$T = 303$ K								
1	0.0000	1156	0.9903	0.0000	1502.74	0.1900	0.4780	69.15
2	0.0854	1174	0.9944	−0.0024	1528.44	0.1913	0.4616	70.63
3	0.1737	1192	0.9984	−0.0045	1555.01	0.1927	0.4446	72.16
4	0.2649	1211	1.0025	−0.0061	1582.47	0.1941	0.4271	73.74
5	0.3592	1230	1.0066	−0.0073	1610.90	0.1955	0.4091	75.37
6	0.4567	1249	1.0107	−0.0081	1640.32	0.1970	0.3904	70.07
7	0.5577	1269	1.0148	−0.0085	1670.79	0.1985	0.3712	78.82
8	0.6623	1288	1.0189	−0.0081	1702.04	0.2000	0.3520	80.62
9	0.7708	1307	1.0230	−0.0072	1734.48	0.2015	0.3327	82.51
10	0.8833	1324	1.0272	−0.0049	1767.12	0.2031	0.3152	84.46
11	1.0000	1335	1.0313	0.0000	1798.66	0.2047	0.3038	86.48
$T = 313$ K								
1	0.0000	1101	0.9879	0.0000	1485.50	0.1900	0.5265	69.17
2	0.0854	1123	0.9920	−0.0034	1512.86	0.1914	0.5073	70.64
3	0.1737	1146	0.9960	−0.0062	1541.13	0.1927	0.4873	72.15
4	0.2649	1169	1.0000	−0.0084	1570.34	0.1941	0.4666	73.72
5	0.3592	1192	1.0041	−0.0100	1600.55	0.1955	0.4451	75.34
6	0.4567	1216	1.0081	−0.0109	1631.80	0.1969	0.4228	77.02
7	0.5577	1240	1.0122	−0.0112	1664.15	0.1984	0.3996	78.75
8	0.6623	1264	1.0162	−0.0108	1697.55	0.1999	0.3755	80.55
9	0.7708	1288	1.0203	−0.0093	1731.85	0.2014	0.3520	82.42
10	0.8833	1311	1.0244	−0.0066	1766.90	0.2030	0.3286	84.35
11	1.0000	1325	1.0285	0.0000	1799.69	0.2046	0.3142	86.36

the present binary mixtures. Similar temperature dependence has been reported by Mariglino *et al.* [18] for formamide + alcohol mixture and Gupta *et al.* [9] for THF + alcohols. Absolute value of $\Delta\eta$ is less in (D + AA) mixture as compared to (D + PA) mixture, which indicates that dispersive forces are predominant in (D + PA) mixture. Many workers [19,20] have reported similar behaviour where negative values of $\Delta\eta$ indicates dispersive interactions.

The ultrasonic velocity in a mixture is mainly influenced by its molecular property. As the simplest molecular property is the free length between the surfaces of the molecules, it seems interesting to find out the variation of intermolecular free length with concentration and temperature. Also molecular radius and relaxation strength are useful in prediction of molecular properties of liquid mixtures. In order to explain the physico-chemical behaviour of the mixtures, we have also evaluated excess
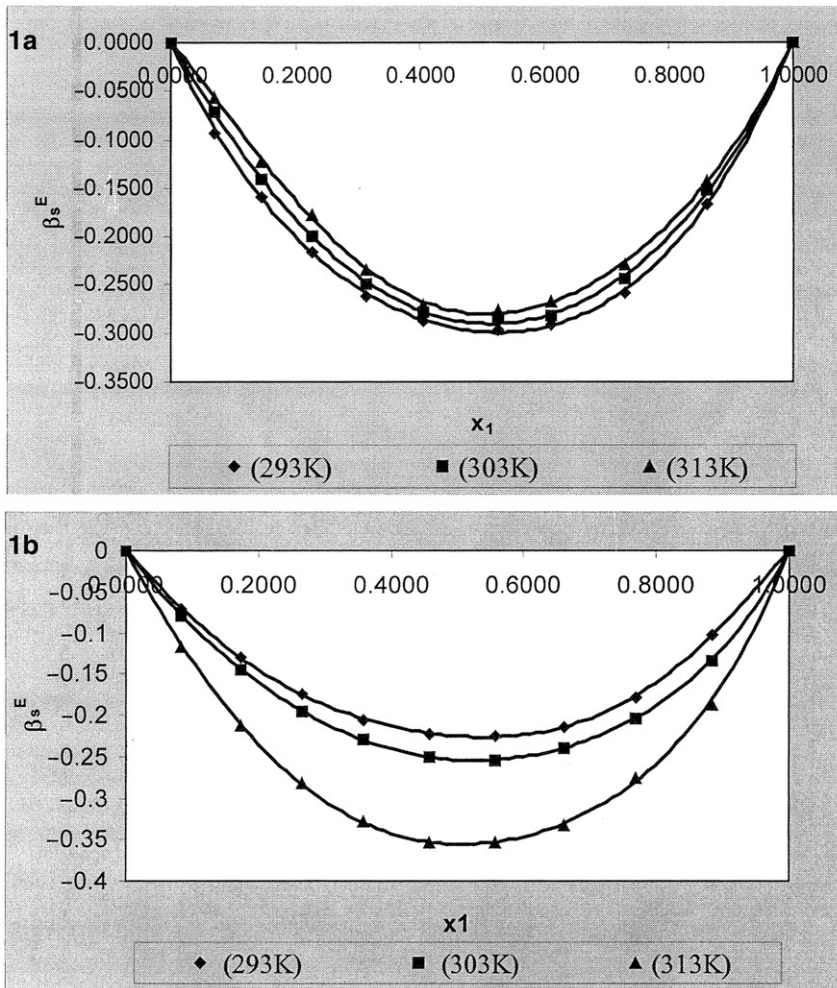
Figure 1. (a) Excess adiabatic compressibility (β_s^E) as a function of dioxane (x_1) for (D + AA) mixture. (b) Excess adiabatic compressibility (β_s^E) as a function of dioxane (x_1) for (D + PA) mixture.

intermolecular free length (L_f^E), molar compressibility (B), molecular radius (r_m), relaxation strength (r), and van der wall's constant (b). L_f^E, B, r and b show non-linear behaviour with mole fraction as can be seen from tables 1 and 2. The excess intermolecular free length (L_f^E) has been found to be negative for both the binary mixtures. The negative intermolecular free length indicates that the sound wave needs to cover a large distance. This again supports the possibility of interaction due to hydrogen bonding between unlike molecules.

4. Conclusion

The measured values of ultrasonic velocity and density along with estimated values of various thermo-acoustic parameters suggest the occurrence of complexation and
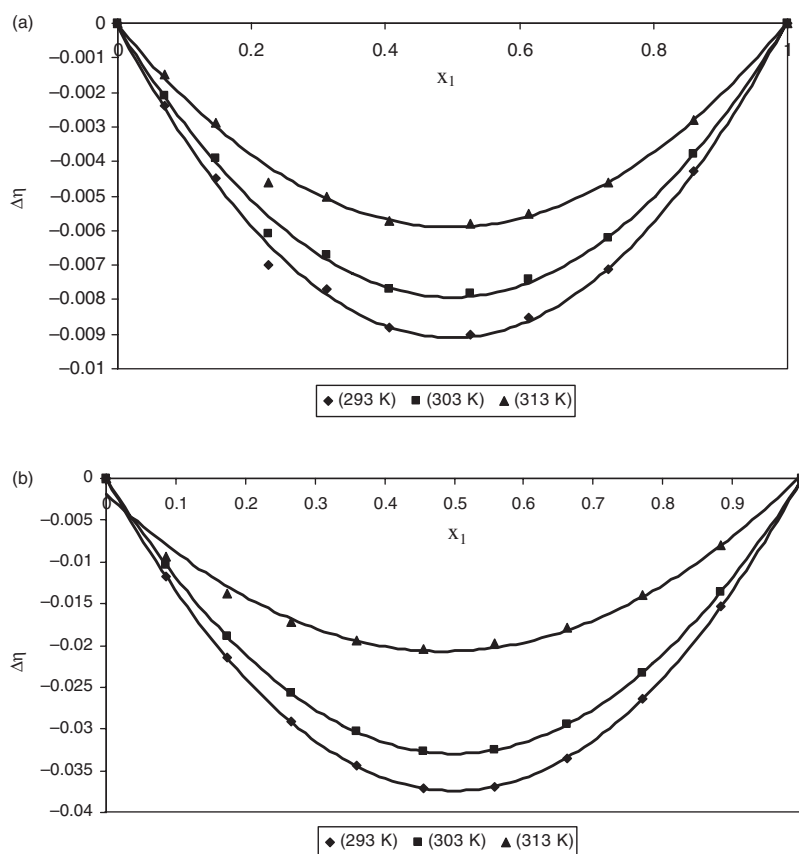
Figure 2. (a) Viscosity deviation ($\Delta\eta$) as a function of dioxane (x_1) for (D + AA) mixture. (b) Viscosity deviation ($\Delta\eta$) as a function of dioxane (x_1) for (D + PA) mixture.

through heteromolecular H-bonding between 1,4-dioxane and carboxylic acids in the two binary mixtures.

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